PREPARATION, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF SILK-METAL-HPMC NANOCOMPOSITE FILMS

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K. V. HARISH

Department of Studies in Physics
Mangalore University
Mangalore, Karnataka – 574 199, INDIA

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Name of the Candidate : **K. V. Harish**

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Name of the research supervisor: Prof. Y. Sangappa

Name of the Institution : **Department of Studies in Physics Mangalore University, Mangalagangotri – 574199**

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SYNOPSIS

The nanocomposite is a multiphase solid material with one, two, or three dimensions of less than 100 nm in one of the phases, or structures having nanoscale repeat distances between the distinct phases that make up the material. To achieve the optimum properties of each component, the material combines one or more individual components. These materials have emerged as viable alternatives to microcomposites and monolithic, but they come with preparation issues related to basic composition and stoichiometry control in the nanocluster phase. These materials have design characteristics and property combinations not present in traditional composites.

Polymer nanocomposites are those polymer matrices that contain organic or inorganic fillers with a homogeneous nanoscale distribution which were prepared by physical blending or chemical polymerizing technologies. These fillers may be nanoparticles, layered materials, fibers, or clusters embedded in a wide variety of natural or synthetic polymers. Nanoparticles have unique electronic, magnetic, thermal, optical, and chemical properties, allowing for new applications in communications, biotechnology, and medicine, as well as photonics and electronics. Metal nanoparticles (Ag, Au, Pt, and Pd) have gained prominence due to their wide range of uses. Physical, chemical, and biological approaches are employed to synthesis metal nanoparticles; however, the yield of nanoparticles is low in the physical technique and the precursor utilized in the chemical technique is harmful to the environment. The biological method provides a clean and environmentally acceptable way for the synthesis of metal nanoparticles, particularly silver and gold nanoparticles, which are of high priority and interest.

Biomaterials have been frequently employed as a biotemplate for the synthesis of silver and gold nanoparticles in recent years. Silk fibroin (SF) and sericin (SS) are two natural protein-polymers derived from the silk cocoons of *Bombyx mori*. The prepared colloidal silk-AgNPs and silk-AuNPs were added to the polymer matrix. Hydroxypropyl methylcellulose (HPMC) is an inert, co-elastic, semi-synthetic biopolymer. It is a solid, white powder and may be shaped into granules. When HPMC is mixed with water it forms colloids. This non-toxic material is combustible and can react vigorously with oxidizing agents. The derivative of cellulose is used in a wide range of application areas such as food, pharmaceutical, textile, and adhesive industries. The HPMC is extensively in use because of its low cost, availability, water-solubility, antimicrobial activity, and non-toxicity. It also has potential application in deep frying food products, drug delivery, and food processing and packaging, also used as a stabilizing agent, protective colloid, thickener, and emulsifier in food industries. In the present work, we have prepared polymer nanocomposite films by blending HPMC with colloidal SF-AgNPs, SF-AuNPs, SS-AgNPs, SS-AuNPs solutions. The new polymer nanocomposite materials will show changed structural, mechanical, thermal, and antibacterial properties which are much different from those conventional materials. In recent years there is a very good scope for the development of hybrid materials for active packaging applications. Combining the characteristics of organic polymers and nanotechnology innovations has led to the creation of new materials with extraordinary properties.

The properties of the prepared HPMC/SF-AuNPs, HPMC/SF-AgNPs, HPMC/SS-AuNPs, and HPMC/SS-AgNPs nanocomposites including optical properties, functional groups, crystallite size, surface morphology, nanoparticles shape, size, and hydrodynamic size of the particles were

studied. To characterize the prepared polymer nanocomposite films, UV-Visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) measurements, scanning electron microscopy (SEM), universal testing machine (UTM), thermogravimetric analysis (TGA), and differential scanning calorimetric (DSC) studies, and potential antibacterial studies were carried out. The study was documented in the form of a thesis, which is subdivided into seven chapters. Each chapter's details are described below.

Outline of the Thesis

The thesis is divided into 7 chapters. The **first chapter** gives a broad overview of polymer nanocomposites, their environmentally friendly fabrication, and their applications. This chapter focused on the historical background of nanocomposite and nanoparticles, particularly Ag and Au. This chapter also clearly explains the general introduction of polymers, biopolymers, and their applications. The general introduction of HPMC and its various applications particularly as food packaging material was also clearly explained in this chapter. A review of literature is included which covering various methods used for the fabrication of polymer nanocomposite particularly HPMC blended with nanomaterial and its properties, morphology, potential bio-applications. The importance and objectives of the present research work have also been discussed in this chapter.

The **second chapter** clearly explains the experimental method and analytical techniques employed for the characterization of the samples. It describes about the preparation method of metal nanoparticles and HPMC/SF-AgNPs, HPMC/SF-AuNPs, HPMC/SS-AgNPs, and HPMC/SS-AuNPs, nanocomposite films. A brief theory/experimental details of analytical instruments like UV-Vis spectroscopy, FT-IR spectroscopy, XRD, SEM, UTM, DSC, and TGA were explained in this

chapter. Detailed protocols for the assessment of the antibacterial activity are also discussed in this chapter.

The **third chapter** explains the preparation of HPMC/SF-AgNPs nanocomposites films and their structural, mechanical, thermal, and antibacterial properties. The existence of silver nanoparticles and increasing in the intensity of the peak in the prepared films was determined by using a UV-Vis spectrophotometer. The functional group present in the HPMC/SF-AgNPs nanocomposites films was determined by FT-IR spectroscopy. The crystalline structure and crystallite size of the prepared HPMC/SF-AgNPs nanocomposites films were determined by XRD measurements. The XRD study revealed the generated AgNPs were FCC crystal structures. The morphology of the HPMC/SF-AgNPs nanocomposites films was determined by using SEM. The mechanical properties of pure HPMC and prepared HPMC/SF-AgNPs nanocomposites films were examined by using UTM. The thermal properties of pure HPMC and prepared HPMC/SF-AgNPs nanocomposites films were determined by using DSC/DTG and TGA studies. The antibacterial properties of prepared HPMC/SF-AgNPs nanocomposites films were also studied by the disc diffusion method. The tested nanocomposites were not sensitive for all the tested bacteria. The zone of inhibition value is very active in the case of *P. aeruginosa*. The detailed investigation and study of bio-applications of HPMC/SF-AgNPs nanocomposites films particularly related to food packaging were also discussed in this chapter.

The **fourth chapter** elucidates the fabrication of HPMC/SF-AuNPs nanocomposites films and the characterization of their properties. The influence of the addition of SF-AuNPs to HPMC on the structural, mechanical, thermal, and antibacterial properties of pure HPMC and HPMC/SF-AuNPs was studied and documented in this chapter. UV-Vis spectroscopy reveals the presence of gold

nanoparticles by showing the localized surface Plasmon resonance at λ=544 nm. It also shows that as the volume of SF-AuNPs varies the absorption band also increased. The crystalline aspects of nanocomposite films were studied by the XRD method. The functional group and the structure of fibroin proteins present in the HPMC/SF-AuNPs nanocomposite films with different compositions were examined by FT-IR spectra. It was found that Tyr residues were responsible for the conversion of gold ions to gold neutral atoms. The surface morphology of the polymer nanocomposite film showed roughness in comparison with pure SF film. The mechanical properties were calculated using UTM. The results show that tensile strength, Young's modulus, and elongation at break (%) were moderate. The native HPMC showed a tensile strength of 33.82±6.8 MPa and the HPMC/SF-AuNPs (18:02) nanocomposite exhibited 28.43±5.43 MPa. The mechanical properties of the nanocomposites are ideal for packing applications. The antibacterial studies showed that prepared HPMC/SF-AuNPs nanocomposite films were very active against all the tested bacteria. The detailed work carried out was presented in this chapter.

The preparation and characterization of HPMC/SS-AgNPs nanocomposites films were studied in the **fifth chapter.** The UV-Vis spectroscopy shows the presence of silver nanoparticles in the prepared HPMC/SS-AgNPs by showing the SPR band at λ=423 nm. The XRD study shows that the crystallite size increased as the blending ratio increased. The surface morphology and presence of silver nanoparticles in the HPMC/SS-AgNPs nanocomposites films were determined by SEM and the study revealed that AgNPs were uniformly distributed in the matrix. The mechanical properties of the HPMC/SS-AgNPs nanocomposites films were determined by using a universal testing machine. The result shows that the mechanical property increases with increasing ratios of SS-AgNPs. The prepared HPMC/SS-AgNPs nanocomposite films were screened against human

pathogens for their antibacterial applications. The study showed that at lower concentrations, the zone of inhibition was not effective. Also, it is important to mention here that the nanocomposites were partially active against gram-negative bacterial species.

The **sixth chapter** explains the development and characterization of HPMC/SS-AuNPs nanocomposites films. The characterization techniques like UV-Vis spectroscopy, XRD, SEM confirms the generation/presence of AuNPs in the nanocomposites films. Mechanical properties of HPMC/SS-AuNPs nanocomposites films were determined by using a UTM. The results show that mechanical properties increase with increasing ratios of SS-AuNPs. This shows that prepared HPMC/SS-AuNPs nanocomposites films have very good applications in food packaging. The TGA, DSC, and DTG experiments were carried out to detect the thermal stability of the pure HPMC and HPMC/SS-AuNPs nanocomposite films. The results show that the addition of SS-AuNPs to the HPMC polymer enhances the thermal stability of the HPMC polymer matrix. The prepared HPMC/SS-AuNPs nanocomposites films were tested against human pathogen bacteria for their potential antibacterial applications. The results showed that nanocomposites are effective against only *S. aureus* (Gram-positive) and *P. aeruginosa* (Gram-negative) bacteria.

The overall summary and conclusions of the studies carried out and suggestions for future work are given in the **seventh chapter**. Most of these results and discussions have been published or communicated in proceedings/journals.

LIST OF PUBLICATIONS OF THE AUTHOR

In Journals/Conference Proceedings

1. Structural, Mechanical and Antibacterial Properties of HPMC/SF-AgNPs Nanocomposite Films. **K. V. Harish,** B. Lakshmeesha Rao, S. Asha, C. Vipin and Y. Sangappa, AIP Conference Proceedings 1942, 050117 (2018): DOI: 10.1063/1.5028748.
2. Structural, Mechanical and Antibacterial Properties of HPMC/SS-AgNPs Nanocomposite Films. **K. V. Harish,** B. Lakshmeesha Rao, S. Asha, A. Suzna and Y. Sangappa, AIP Conference Proceedings 2220, 020156 (2020): DOI: 10.1063/ 5.0001156.
3. Effect of Gamma Irradiation on HPMC/ZnO Nanocomposite Films. B. Lakshmeesha Rao, S. Asha, R. Madhukumar, S. Latha, Mahadeva Gowda, G. Rajesha Shetty, C. S. Shivananda, **K. V. Harish** and Y. Sangappa, AIP Conference Proceedings 1665, 070020 (2015): DOI: 10.1063/1.4947884.
4. Structural and Thermal Properties of Gamma Irradiated *Bombyx mori* Silk Fibroin Films. R. Madhukumar, S. Asha, B. K. Sarojini, R. Somashekhar, B. Lakshmeesha Rao, C. S. Shivananda, **K. V. Harish** and Y. Sangappa, AIP Conference Proceedings 1665, 070025 (2015): DOI:10.1063/1.4947889.
5. UV Irradiation Effects on HPMC-ZnO Nanocomposites. B. Lakshmeesha Rao, C. S. Shivananda, R. G. Shetty, R. Madhukumar, S. Latha, Mahadeva Gowda, **K. V. Harish** and Y. Sangappa, Proceedings of International Conference on Advances in Materials, Manufacturing and Applications (AMMA 2015), ISBN 978- 93-84743-68-0 2015.
6. Influence of UV Irradiation on Hydroxypropyl Methylcellulose Polymer Films. B. Lakshmeesha Rao, C. S. Shivananda, G. Rajesha Shetty, **K. V. Harish**, R. Madhukumar

and Y. Sangappa, AIP Conference Proceedings 1953, 080011 (2018): DOI: 10.1063/1.5032817.

7. Synthesis of Gold Nanoparticles Using Silk Fibroin and their Characterization. Mahadeva Gowda, K. S. Harisha, T. Ranjana, **K. V. Harish**, B. Narayana, K. Byrappa and Y. Sangappa, AIP Conference Proceedings 1953, 030184 (2018): DOI: 10.1063/1.5032519.

PRESENTATIONS IN CONFERENCE/SYMPOSIA

1. Gamma Irradiation Effects on HPMC-ZnO Nanocomposites. B. Lakshmeesha Rao, R. Madhukumar, C. S. Shivananda, R. G. Shetty, **K. V. Hareesh** , S. Asha and Y. Sangappa, Third International Conference on Polymer Processing and Characterization – 2014. Kottayam, November 11-13, (2014).
2. Effect of Gamma Irradiation on HPMC/ZnO Nanocomposite Films. B. Lakshmeesha Rao, S. Asha, R. Madhukumar, S. Latha, Mahadeva Gowda, G. Rajesha Shetty, C. S. Shivananda, **K. V. Harish** and Y. Sangappa, In DAE-Solid State Physics Symposium – 2014. Vellore Institute of Technology, Vellore, December 16-20, (2014).
3. Structural and Thermal Properties of Gamma Irradiated *Bombyxmori* Silk Fibroin Films. R. Madhukumar, S. Asha, B. K. Sarojini, R. Somashekhar, B. Lakshmeesha Rao, C. S. Shivananda, **K. V. Harish** and Y. Sangappa, In DAE-Solid State Physics Symposium – 2014. Vellore Institute of Technology, Vellore, December 16 - 20, (2014).
4. Synthesis and Characterization of CdS Nanoparticles. **K. V. Harish**, B. Lakshmeesha Rao, C. S. Shivananda, B. K. Sarojini and Y. Sangappa, International Conference on Nanostructured Polymeric Materials and Polymer Nanocomposites–2015. Mahatma Gandhi University, Kottayam, November 13-15, (2015).

5. Structural and AC Conductivity Property of Silk Fibroin – Silver Nanoparticles (SF-AgNPs) films. C. S. Shivananda, B. Lakshmeesha Rao, **K. V. Harish**, Y. Wang and Y. Sangappa, International Conference on Nanoscience, Nanotechnology & Advanced Materials – 2015. Gitam University, Visakapatnam, December 14 - 17, (2015).
6. Synthesis and Characterization of CdS Nanoparticles. **K. V. Harish**, B. Lakshmeesha Rao, C. S. Shivananda, B. K. Sarojini and Y. Sangappa, FuNEH-2016. Mangalore University, Mangalagangotri, Karnataka, March 21-22, (2016).
7. A Study of Surface Wettability and Antibacterial Activity of HPMC/ZnO BNCs for Food Packaging Application. B. Lakshmeesha Rao, R. Madhukumar, C. S. Shivananda, G. Rajesha Shetty, **K. V. Harish**, R. Neelakandan and Y. Sangappa, FuNEH – 2016. Mangalore University, Mangalagangotri, Karnataka, March 21-22, (2016).
8. Preparation and Characterization of HPMC/SF-AuNPs, Nanocomposite Films. **K. V. Harish**, B. Lakshmeesha Rao, S. Asha and Y. Sangappa, PAIR-2017. Mangalore University, Mangalagangotri, Karnataka, April 11-13, (2017).
9. Preparation and Characterization of HPMC/SF-AuNPs Nanocomposite Films. **K. V. Harish**, B. Lakshmeesha Rao, S. Asha and Y. Sangappa Polycon-2017. SJCE, Mysore, September 15-16, (2017).
10. Synthesis of Gold Nanoparticles Using Silk Fibroin and their Characterization. Mahadeva Gowda, K. S. Harisha, T. Ranjana, **K. V. Harish**, B. Narayana, K. Byrappa and Y. Sangappa, ICC -2017. Bikaner, November 24-25, (2017).

11. Structural, Mechanical and Antibacterial Properties of HPMC/SF-AgNPs Nanocomposite Films. **K. V. Harish,** B. Lakshmeesha Rao, S. Asha, C. Vipin and Y. Sangappa, DAE, SSP-2017. December 26-30, (2017).

12. Structural, Mechanical and Antibacterial Properties of HPMC/SS-AuNPs Nanocomposite Films. **K. V. Harish,** B. Lakshmeesha Rao, S. Asha, A. Suzna and Y. Sangappa, ICC, Bikaner-2019. October 14-15, (2019).

Dr. Y. Sangappa
Research Supervisor
Date:

K V Harish
Research Student